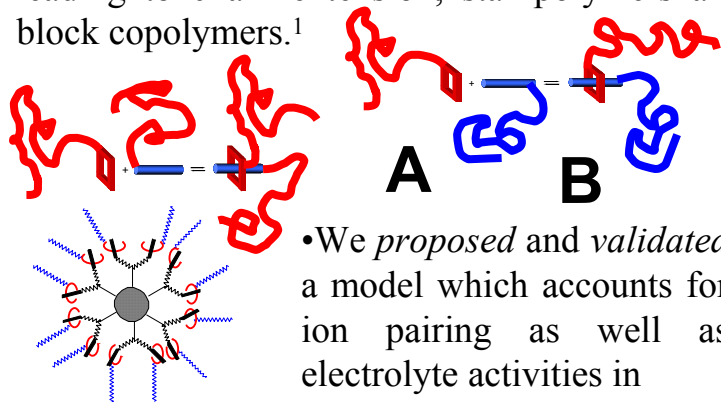


# SUPRAMACROMOLECULES: STRUCTURE/PROPERTY CONTROL VIA SELF-ASSEMBLY WITH WELL-DEFINED MACROMOLECULES

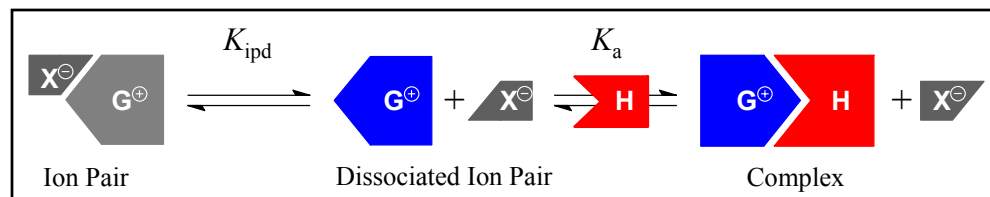
Harry W. Gibson, DMR-0097126

- We *developed* methods for synthesis of narrow molecular weight polymers with host or guest end groups.<sup>1</sup> Using controlled free radical methods we prepared polystyrenes with dibenzo-24-crown-8 and bis(*m*-phenylene)-32-crown-10 host end groups and paraquat guest end groups.<sup>1</sup> By anionic techniques polystyrene and polyisoprene were fitted with dibenzylammonium guest end groups.<sup>1</sup>

- We *demonstrated* by viscometry that these end-functionalized polymers self-assemble selectively via pseudorotaxane formation, leading to chain extension, star polymers and block copolymers.<sup>1</sup>

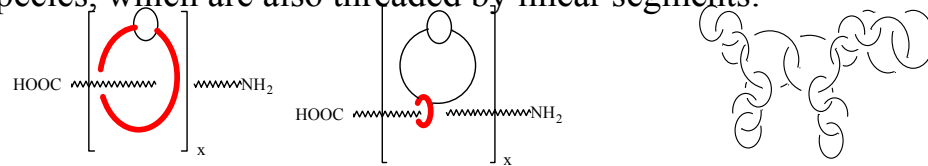


- We *proposed* and *validated* a model which accounts for ion pairing as well as electrolyte activities in



host/guest systems (above).<sup>2</sup> Association constants for complex formation ( $K_a$ ), ion pair dissociation constants ( $K_{ipd}$ ), and activity coefficients may be readily *derived* from a series of well-designed experiments.

- We *showed* that synthesis of aramides from large crown ether diacids leads to the formation of pseudorotaxane, rotaxane and catenane structures as a result of self-threading of the crown ether rings, combined with extensive formation of cyclic polymeric species, which are also threaded by linear segments.<sup>3</sup>



The degree of polymerization,  $n$ , in a self-assembled polymer is highly dependent upon  $K_a$ ,  $n \sim 2K_a^{1/2}[M]^{1/2}$ , in which  $[M]$  is the monomer concentration; thus at 1 M to achieve  $n = 100$ ,  $K_a \geq 2500 \text{ M}^{-1}$ . The commonly available pseudorotaxane systems do not meet this requirement,  $K_a < 1000 \text{ M}^{-1}$ .

- (1) (a) H. W. Gibson, Z. Ge, F. Huang, J. W. Jones, H. Wang, A. Farcas, *Polym. Preprints* **2002**, 43(1), 611-612. (b) H. W. Gibson, Z. Ge, F. Huang, J. W. Jones, H. Wang, A. Farcas, *Polym. Preprints* **2003**, 44(2), 475-476.
- (2) a) J. W. Jones, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, 125, 7001-7004. b) F. Huang, J. W. Jones, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, 125, 14458-14464. c) J. W. Jones, M. A. G. Berg, F. Huang, H. Wang, B. F. Habenicht, H. W. Gibson, *J. Am. Chem. Soc.*, to be submitted.
- (3) H W. Gibson, D. S. Nagvekar, N. Yamaguchi, S. Bhattacharjee, H. Wang, M. J. Vergne, D. M. Hercules, *Macromolecules*, in press.

• To increase  $K_a$ , based on analyses of X-ray structures, we *designed, synthesized and characterized* a series of new hosts that are preorganized and possess additional binding sites. Notable examples are provided by the cryptands **1** and **2**. **1** very strongly binds paraquat **3**,  $K_a = 5.0 \times 10^6 \text{ M}^{-1}$ ! Its X-ray structure (below) shows the interaction between the pyridyl N and the  $\beta$ -protons of the guest; this system should be capable of producing supramolecular polymers with more than 2000 repeat units! New host **2**, synthesized in very high yield, also binds guest **3** strongly,  $K_a = 1.0 \times 10^4 \text{ M}^{-1}$ .

## Broader Impacts of NSF Award, Harry W. Gibson, DMR-0097126

### Scholarship

- 7 undergraduates (4 females) have actively participated in research since 2000
- 19 refereed papers and 6 preprints since 2000 based on DMR funding
- 1 US patent based on DMR funding
- 38 presentations, including 21 invited lectures (at universities, national and international meetings) since 2000 based on DMR funding
- 3 M. S. degrees awarded (Jason W. Jones, Feihe Huang, Amy Fletcher) and 1 Ph. D. degree (Jason W. Jones) since 2000 under DMR funding
- 5 postdocs (2 females) involved to various extents since 2000 under DMR funding

### Awards

- William Preston Award, best Master's Thesis at Virginia Tech, 2003, Feihe Huang, current Ph.D. candidate
- DOE Travel Award to Attend the 53<sup>rd</sup> Annual Meeting of Nobel Laureates, 2003, Jason W. Jones
- 2 Departmental Graduate Research Excellence Awards: Jason W. Jones (2003), Feihe Huang (2004)
- Cook Faculty Research Award, VT Chemistry Department, 2001, Harry W. Gibson
- Alumni Award for Research Excellence, Virginia Tech, 2004, Harry W. Gibson

**Industrial Connection:** LUNA Innovations, Inc.

